SENSOR FOR COMBUSTIBLE GASES
WITH SENSIBLE ELEMENT OXIDE SEMICONDUCTOR SnO₂
OBTAINED BY SOL GEL METHOD

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The sensor for the combustible gases consists in a tubular substrate of alumina
where inside was placed the heater a coil of Pt and at the surface the sensible element
deposited by spin coating in 200 nm thickness. The oxidic element SnO₂-doped Pd is
obtained by sol gel method and heat treated at 600°C. The sensible element has a
mesoporous material with a hexagonal ordinate structure and a specific surface area by
456 m²/g with the dimensions of the pores of 27.8 Å. The supply alimentation of the
heater was 5 V with a operating temperature of 200°C and for 100% LIE CH₄ and C₃H₈
the sensibilities were 60% and respectively 75% and the response time was 30 seconds.

Key words: semiconductor oxide gas sensor, sol gel method, surfactant,
combustible gases, adsorption isotherm, scanning electron
microscopy, tunneling electron microscopy.

1. INTRODUCTION

Among the semiconductor oxide, for gas sensors, SnO₂, is the most widely
used to detect reducing gases such as H₂, CO, hydrocarbon and the alcohol [1, 2].
The application of pure SnO₂ gas sensors is limited because of the poor
selectivity to a particular gas. To improve the sensing property, SnO₂ was
generally doped with transition metals, such as Pt, Pd, Ag [3, 4]. The oxide SnO₂
is a n-type semiconductor with a wide band gap of about 3.6 eV. At the edge of
the conduction band the calculated density of states derived from atomic Sn 5s
state, is low. Correspondingly the measured Hall mobility of bulk electrons in
single crystals are reasonably high, 80 and 200 cm²/Vs at 500 K and 300 K,
respectively. The edge of the valence band emerges from O 2p orbital, which are
directed perpendicular to the Sn-O bond (lone pair orbitals). At temperature
above about 800 K, the concentration of oxygen vacancies and the conductance
depend on the oxygen pressure.

\[ \sigma \sim P_{O_2}^{-1/m} \]  

(1)

where: \( \sigma \) is the oxide conductivity, \( P_{O_2} \) is the oxygen partial pressure and the experimental value \( m = 6 \) corresponds to a double ionized oxygen vacancy \((V_O)^{2+}\). This vacancy acts as a donor with an energy level 150 MeV below the conduction band. The conductivity of SnO\(_2\) can be increased by same substitution impurities such: fluorine on an oxygen site or antimony on a tin site, which also act as shallow donors. The electron concentration near the semiconductor surface varies with the density and occupancy of surface acceptors and donors. In a gas sensor this density of surface states depend on surface reaction with ambient gas. The principle of gas detection consists in the reversible process of oxidation/reduction at the oxide surface and results in a modification of the carrier density and hence a change in a resistance of this n-type semiconductor. The oxidizing property of SnO\(_2\) is usually explained by the involvement O\(^-\) and O\(_2^-\) species existing on the surface [5].

Such sensing mechanism in detection of the CH\(_4\), the main products obtained from the reaction between CH\(_4\) and SnO\(_2\) are CO\(_2\) and H\(_2\)O. Above 230°C, CO\(_2\) and H\(_2\)O appear as decomposition products (exposure time: 20 minutes). So, it is assumed that the following reactions will take place when CH\(_4\) adsors on the surface of SnO\(_2\). The lattice oxygen, \( O_{lat} \) of SnO\(_2\) can also be reactive with methane gas, at least in part due to its high concentration. However, in the presence of O\(_2\), as in the practical operating conditions of gas sensors, the adsorbed oxygen O\(_2^-\) and O\(^-\) on the surface of SnO\(_2\) are by far the move active forms. In this case, the following reactions are assumed:

1. \[
\text{CH}_4(\text{gas}) + 2O_{lat} \rightarrow \text{CH}_3 - O_{lat} + H - O_{lat} \tag{2}
\]
2. \[
\text{CH}_3 - O_{lat} + 2O_{lat} + 2O^- \rightarrow \text{CO}_2(\text{gas}) + 3H - O_{lat} + 2e^- \tag{3}
\]
3. \[
\text{CH}_3 - O_{lat} + CH_3 - O_{lat} + O^- \rightarrow H_2\text{O(gas)} + C_2\text{H}_4(\text{gas}) + 2O_{lat} + e^- \tag{4}
\]

In our work we present the configuration of the sensor, the method for the syntheses of the SnO\(_2\)-Pd by sol gel and the morphological-structural characterization of the sensing material and the characteristic of the sensor in CH\(_4\) and C\(_3\)H\(_8\) atmospheres.

2. EXPERIMENTAL

Fig. 1 shows the schema of the element sensible obtained by sol gel method. As precursor for the SnO\(_2\) preparation one utilizes SnCl\(_4\)·5H\(_2\)O and
Sensor for combustible gases with semiconductor SnO$_2$

Fig. 1. – Schema for SnO$_2$ preparation by sol gel method.

Surfactant cetyltrimethylammonium bromide under a hydrothermal treatment at 80°C for 3 hours. The obtained powder was heat treated at 600°C and impregnated with a 1% PdCl$_2$ solution.

The support is constituted by the tubular alumina with the dimensions: $\phi_{\text{ext}} = 2.2$ mm, $\phi_{\text{int}} = 0.8$ mm $l = 6.2$ mm, obtained by sintering method. The sensible element is composed from semiconductor oxide SnO$_2$ doped Pd deposited by the support by spin coating method in 200 nm thickness and heat treated at 600°C from 1 hour.
The heater is composed by a coil with 5 turns of KANTAL and introduce inside of the support. The sensor is monted on the sticlotextolit support by the electric contacts and pins. Fig. 2 shows the sensor configuration.

3. RESULTS AND DISCUSSION

$N_2$ adsorption, which is widely used method to characterize the surface area and pore size distribution of porous materials, was used in this work. $N_2$ adsorption was performed using $N_2$ at liquid temperature as an adsorbate. The surface area was determined by a multipoint BET method in the partial pressure range $P/P_0$ of 0.05–0.25. Fig. 3 shows the $N_2$ adsorption and desorption isotherms of calcined, SnO$_2$.

![Fig. 2. – Configuration of the sensor for combustible gases 1. Support, 2. Heater, 3. Oxide sensible element, 4. Connector.](image)

![Fig. 3. – Adsorption isotherm of SnO$_2$.](image)

![Fig. 4. – Distribution of pores dimensions for SnO$_2$ obtained by sol gel.](image)
which surfactant had been removed by calcination at 600°C. Desorption isotherm was used to determine the pore size distribution. SnO$_2$ has a high surface area 456 m$^2$/g and a pores diameter of 27.8 Å and a high pores volume. The structure is specific of mesoporous materials with a ordinate hexagonal structure. The pore diameter distribution is shown in Fig. 4. The sharp pore diameter distribution at about 28 Å indicating the uniform mesoporous structure of SnO$_2$ obtained by sol gel method.

The results obtained for the porous structure were confirmed by electronic microscopy SEM and TEM. Fig. 5 and Fig. 6 show the images SEM and TEM for SnO$_2$ and indices a typical structure of molecular sieves.

SnO$_2$ presents on the amorph fund and the ordinate zones with hexagonal organization of the pores.

The detection characteristics are:
- Range detection: 0–100% LIE (lower limit of detection)
- Supply alimentation heater: 5 V
- Resistance in air: 295 kΩ
- Resistance in air at function temperature: 6.6 kΩ at 5 V
- Function temperature: 200°C

The sensitivity is given by the relation:

$$S = \frac{R_a - R_g}{R_a} \times 100$$  \hspace{1cm} (5)

where:
- $R_a$: resistance in air, kΩ
- $R_g$: resistance in gas, kΩ.
For 100% LIE gas the sensitivities were 60% for CH\textsubscript{4} and 75% for C\textsubscript{3}H\textsubscript{8}. The response time was 30 seconds.

Fig. 7 shows the characteristic sensitivity-rate gas for sensor exposure to atmospheres of CH\textsubscript{4} and C\textsubscript{3}H\textsubscript{8}. The response time of the sensor was 30 seconds.

4. CONCLUSIONS

A combustible gases sensor based on SnO\textsubscript{2} doped Pd is made. The sensible element was obtained by sol gel method utilizing the surfactant cetyltrimethylammonium bromide and precursor SnCl\textsubscript{5} \cdot 5H\textsubscript{2}O under a hydrothermal regime at 80°C heat treated at 600°C. Specific area is 456 m\textsuperscript{2}/g and the pores diameter was 27.8 Å. Adsorption isotherm, SEM and TEM images shows a mesoporous structure with a hexagonal ordinate type molecular sieve. The working temperature of the sensor was 200°C for a alimentation supply of 5 V, the resistance in air at the function temperature was 6.6 kΩ which decrease in gases atmosphere. For 100% LIE gas the sensitivities were 60% for CH\textsubscript{4} and 75% for C\textsubscript{3}H\textsubscript{8} and the response time was 30 seconds.

REFERENCES


